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Aggregation of fullerene (C_{60}) nanoparticle: A molecular-dynamic study*

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We present the results of molecular dynamics simulations of net positively charged fullerene nanoparticles in salt-free and salt-added solution. The aggregation of fullerene (C_{60})-like nanoparticle and counterion are studied in detail as a function of temperatures and a finite salt concentration. Our simulations show that the strong conformation changes as temperature changes. The net positively-charged nanoparticles do not repel each other but are condensed under proper temperatures. If salts are added, the aggregated nanoparticles will be disaggregated due to the Debye screening effect.

Keywords: nanoparticle, molecular dynamics simulation, aggregation, counterion release

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1. Introduction

Nanotechnology has vast potential in uses such as fuel cells, microreactors, drug delivery devices, and personal care products.[1] The fullerene C_{60} is one type of manufactured nanoparticle. Fullerenes are lipophilic and localized into lipid-rich regions such as cell membranes in vitro. The mechanism of the nanoparticle synthesis is still unclear.[2,3] However, it has been found that C_{60} molecules tend to aggregate in different solvents.[4,5] It is assumed that the fullerene nanoparticle formation process involved the aggregation of C_{60} molecules. Nanoparticle aggregation is of major importance in biomedicine, yet it is not well understood. Several studies have pointed out the toxicity of fullerene nanoparticles on microbes and human cells.[6,7] While the mechanism of the toxicity of fullerene nanoparticles is still being discussed,[8] the condensation state of the nanoparticles may play a role in determining its level of toxicity. However, these mechanisms are yet to be verified in the case of fullerene nanoparticles. The aggregation and deposition kinetics of fullerene nanoparticles in the presence of monovalent electrolytes have been investigated by employing experiments. It is pointed out that electrostatic double layer repulsion controls their aggregation and deposition kinetics as predicted by the DLVO theory.[1,9]

This paper deals with the phase transitions, self-assembly, and aggregation of nanoparticles in solution. we present a computer simulation study of nanoparticles aggregation. Our work is aimed to study nanoparticles aggregation from the way which refers like-charged nanoparticle attraction as a result of strong electrostatic correlations in the presence of counterions or at low temperatures. The paper is organized as follows. The simulation model is introduced in Section 2. Subsection 3.1 shows the simulation results and discussion for salt-free condition. Effects of added salt are discussed in Subsection 3.2. Our conclusions are presented in Section 4.

2. Models and simulation methods

A fullerene-like sphere, which consists of 60 beads, was used to represent fullerene nanoparticle (see Fig. 1). The diameter of each nanoparticle is equaled with 17.4 Å. The charges on the nanoparticle surface are strongly nonuniformly distributed, while they are net positively charged. Nanoparticles are surrounded by their neutralizing counterions. The LAMMPS molecular dynamics package[10] was used to carry out the simulations.

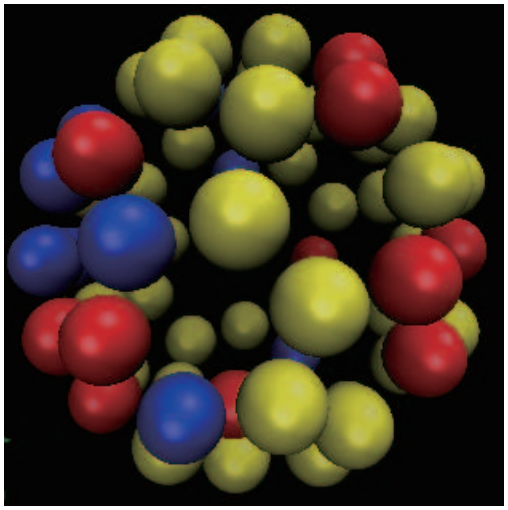

Fig. 1. (color online) C_{60} fullerene-like nanoparticle with negatively charged segment (in blue color) and positively segment (in red color). Yellow bead denotes neutral segment.

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The total interaction potential was composed of four contributions:

$$U_{\rm tot} = U_{\rm LJ} + U_{\rm Coul}. \tag{1}$$

The nanoparticles were assumed to be in athermal solvent, modeled by a purely repulsive short-range Lennard–Jones potential, cut at its minimum:

$$U_{\rm LJ}(r) = 4\varepsilon\left[\left(\frac{\rm d}{r}\right)^{12} - \left(\frac{\rm d}{r}\right)^{6} - \left(\frac{\rm d}{r_{\rm c}}\right)^{12} + \left(\frac{\rm d}{r_{\rm c}}\right)^{6}\right]. \tag{2}$$

The cutoff radius was $r_{\rm c} = 2^{1/6}d$, d being the size of the bead and ε the potential depth. The latter was of no significance here because of the athermal solvent assumption. The Coulomb interaction is of long range and has to be addressed with particular care. The simulation package LAMMPS includes the implementation of the particle–particle/particle–mesh (PPPM) algorithm[11] that solves the field equation on a lattice through fast Fourier transformation. In this way, the influence of periodic images of charged particles were properly accounted for. Formally, the Coulomb potential is written as

$$U_{\rm Coul}(r) = l_{\rm B}k_{\rm B}T \sum_{n_x=-\infty}^{\infty}\sum_{n_y=-\infty}^{\infty}\sum_{n_z=-\infty}^{\infty}\sum_{i=1}^{N_{\rm tot}-1}\sum_{j=i-1}^{N_{\rm tot}} \times \frac{q_i q_j}{|\boldsymbol{r}_{ij} + n_x L\boldsymbol{e}_x + n_y L\boldsymbol{e}_y + n_z L\boldsymbol{e}_z|}, \tag{3}$$

where q_i and q_j are the corresponding charges and $l_{\rm B} = e^2/4\pi\varepsilon_0\varepsilon k_{\rm B}T$, the Bjerrum length,[12] defines the distance at which both Coulomb energy and thermal energy ($k_{\rm B}T$) are of the same magnitude. $\boldsymbol{e}_x$, $\boldsymbol{e}_y$, and $\boldsymbol{e}_z$ are unit vectors in x, y, and z directions, and the indices n_x, n_y, and n_z run over the periodic images of the simulation box. $N_{\rm tot}$ is the total number of charges and L is the box-size in the x, y, z directions.

The equation of motion was defined as a Langevin equation

$$m\frac{{\rm d}^2\boldsymbol{r}_i}{{\rm d}t^2} + \varsigma\frac{{\rm d}\boldsymbol{r}_i}{{\rm d}t} = -\frac{\partial U_{\rm TOT}}{\partial \boldsymbol{r}_i} + \boldsymbol{F}_i, \tag{4}$$

where m is the particle mass and ς the friction constant. $\boldsymbol{F}_i$ is a Gaussian random force used to couple the system to the heat bath, with the correlation function

$$\langle \boldsymbol{F}_i(t)\cdot\boldsymbol{F}_j(t')\rangle = 6mk_{\rm B}T\varsigma\delta_{ij}\delta(t-t'). \tag{5}$$

The temperature was $k_{\rm B}T = 0.6\varepsilon$, and the damping constant $\varsigma = 0.5\tau_{\rm LJ}^{-1}$ with $\tau_{\rm LJ} = (md^2/\varepsilon)^{1/2}$ being the Lennard–Jones time.

3. Results and discussion

3.1. Effects of temperature in salt-free solution

Figure 2 shows nanoparticle-ion conformations at $T = 180$ K, $T = 210$ K, and $T = 270$ K, respectively.

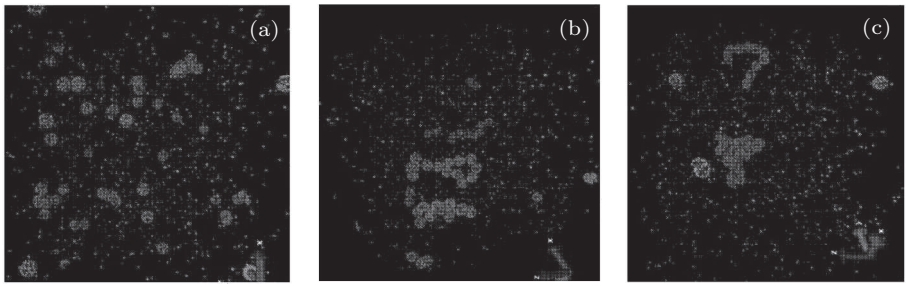

Fig. 2. Scheme of the nanoparticle-ion conformation on different temperatures: (a) $T = 180$ K, (b) $T = 210$ K, and (c) $T = 270$ K.

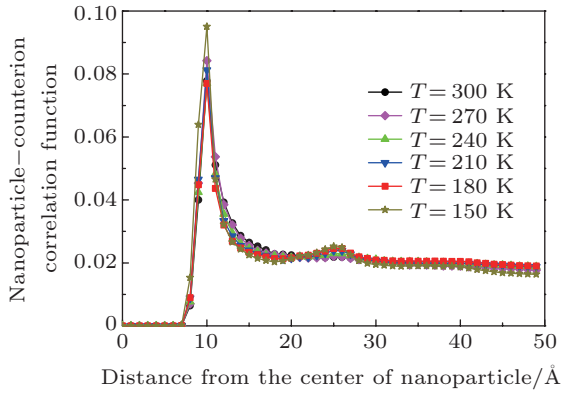

Fig. 3. (color online) Nanoparticle–counterion radius correlation function at different temperatures.

From the pictures, it is easily found that more nanoparticles are aggregated at $T = 180$ K than $T = 210$ K, and $T = 270$ K. The pair correlation function $g(r) \approx n/r^3$ is related to how the particles are packed together for short distances. In Fig. 3 we display nanoparticle–counterion correlation function profile at different temperatures. At distance from the center of nanoparticle $r = 11$ Å, the correlation function reached a maximum value. It means counterions are adsorbed on nanoparticle surface.

One way of thinking about just how strong and how long the interaction range between an ion pair is, is to calculate how far away two charges have to be, so that the attractive energy to drive the charges to a particular configuration is equaled

by the randomizing effects of the thermal energy. The electrostatic interaction in a system with a dielectric constant ε can be characterized in terms of the Bjerrum length $l_B = e^2/4\pi\varepsilon_0\varepsilon kT$, where e is the elementary charge and ε_0 is the vacuum electric conductivity, T is temperature. The Bjerrum length is the separation at which the electrostatic interaction between two ions is comparable in magnitude to KT. If T is lowered, two charges should have stronger interaction. But the nanoparticle–counterion correlation function is not in inverse proportion to temperatures in this picture.

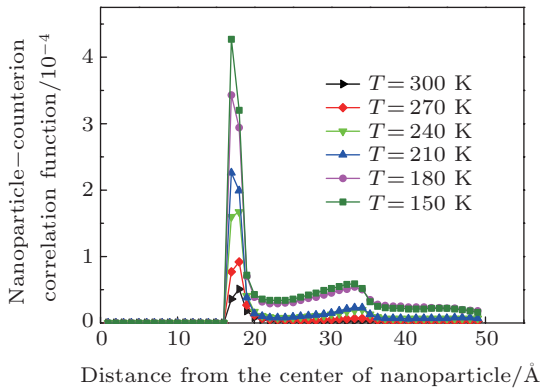

Fig. 4. (color online) Nanoparticle–nanoparticle radius correlation function at different temperatures.

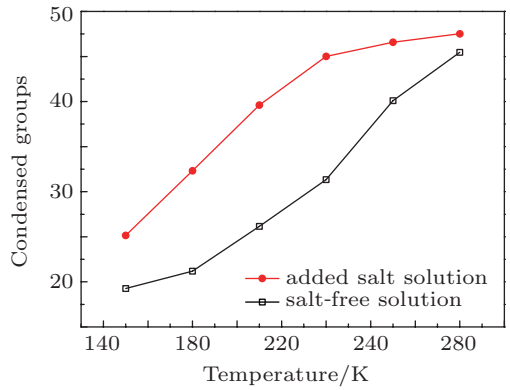

Fig. 5. (color online) Number of condensed nanoparticle groups at different temperatures for added salt solution and salt-free solution.

We show the nanoparticle–nanoparticle correlation function profile at different temperatures in Fig. 4. At distance around 17.4 Å where is the nanoparticle surface, the maximum number of nanoparticles are packed together and the correlation function is clearly in inverse proportion to temperatures. Originally the particle correlation should be more stronger if temperature is lowered. But figures 3 and 4 show different dependence of pair correlation function on temperatures. The reason can be found in Fig. 5. There are positive and negative charges randomly distributed on each nanoparticle. Each particle is surrounded with its counterions. Due to the strong electrostatic attraction, some nanoparticles are aggregated together to replace the original counterions of nanoparticles. The counterions of nanoparticles forming a group are released. So the number of condensed ions around a nanoparticle is not increased along with lowering the temperature.

3.2. Effects of added salt

In solutions, salts are ubiquitously used to control pH, ionic strength, and osomlality in scientific research and industry applications. It is important to understand how salts modulate nanoparticle–nanoparticle interactions, so that the solution behavior such as protein crystallization, precipitation, and solution stability can be controlled. The following set of simulations were carried out at finite salt concentrations. In the present model nanoparticle counterions and salt ions are considered to be identical they are subject to an unrestricted exchange. Interactions between charges are affected and reduced in strength or screened by the presence of salt ions and co-ions. The Debye length is defined as[13]

$$\lambda_D = \frac{1}{\sqrt{4\pi l_B}(2c_s + c_{ci})}, \tag{6}$$

where c_s and c_{ci} are the salt and counterion concentrations respectively. If salts are added, the Debye length is getting smaller. It means the electrostatic interaction is screened by salt ions and counterions. Figure 6 presents nanoparticle–ion correlation function at salt concentration $c_s = 1.2 \times 10^{-5}$ mol/L. Compared with Fig. 3, nanoparticle–ion correlation function is clearly in inverse proportion to temperature. That can be explained from Fig. 5. For the same temperature, fewer nanoparticles are aggregated in salt solution. It means fewer counterions are released between nanoparticles. So more counterions are distributed around nanoparticle surface if temperature is lowered. The nanoparticle–nanoparticle radius correlation function at a finite salt concentration is shown in Fig. 7. The first neighbor distance r_1 is around 17.5 Å, the second neighbor distance r_2 is around 35 Å. The nanoparticle–nanoparticle correlation function does not share an inverse relationship with temperature which can be found in Fig. 4. This is due to Debye-screening effect caused by added salts.

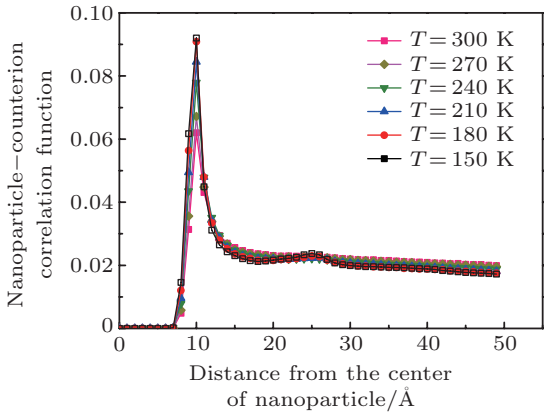

Fig. 6. (color online) Nanoparticle–counterion radius correlation function for different temperatures at salt concentration $c_s = 1.2 \times 10^{-5}$ mol/L.

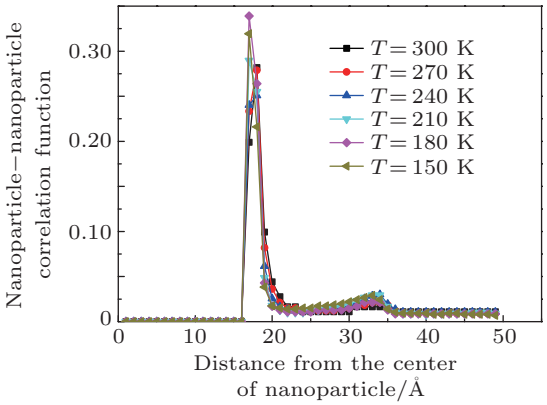

Fig. 7. (color online) Nanoparticle–nanoparticle radius correlation function for different temperatures at salt concentration $c = 1.2 \times 10^{-5}$ mol/L.

4. Conclusion

In this paper, we present a detailed MD simulations study of aggregation and disaggregation of fullerene nanoparticles. The nanoparticles are net positively charged at the studied solution. The effects of temperatures have been investigated. When lowering temperatures, more nanoparticles are aggregated together. The strength of electrostatic interactions is enhanced by maintaining the system at low temperatures. Like-charged nanoparticles attract each other as a result of strong electrostatic correlations at low temperatures. Lowering medium of dielectric constant can also reach the same result. If we add salts into solution, the Debye-screening effect is created by salt ions and co-ions. The strength of electrostatic interaction is reduced. The disaggregation happens if the salt concentration is high enough.

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